Studies on the Nature of the Glass Electrode Potential. III. On the Cause of the Asymmetry Potential of the Glass Electrode.

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According to the so-called Haber theory of the glass electrode, there should exist no potential, when both surfaces of a glass electrode membrane are brought into contact with one and the same solution. Actually, however, a certain potential appears, which is called the asymmetry potential. As to the cause of this potential, some experimental studies were performed by Elder[1], Buchböck[2], and Kahler and DeEds[3], though none of them can be regarded as fundamental. (The Chemical Abstracts recorded a paper by Haugaard[4]. Not having read his paper, however, we must necessarily refrain from commenting upon his conclusions.) In the present investigation, this problem is examined from the point of view of current theories concerning the glass electrode. The experimental methods and the sign of the potential are the same as described in the previous report[5]. Experiments were carried out at 25°C. in most cases.

(1) The Asymmetry Potential and the Difference of Hydrogen Electrode Function on Outer and Inner Surfaces of the Electrode Membrane. The hydrogen electrode functions $\Delta E/\Delta p$H of both the inner and the outer surfaces of the electrode bulb (which serves as the electrode membrane), and its asymmetry potentials in two buffer solutions of pH 3 and 7 were determined after the electrode had been fully equilibrated with water, using many glass electrodes made of commercial soft glass, MacInnes glass, and Morton glass purchased in England. As to the meaning of $\Delta E/\Delta p$H, refer to the previous report[5]. The measurement of $\Delta E/\Delta p$H on both surfaces of the electrode membrane was performed with the two buffer solutions in a way similar to that of Kahler and DeEds[3].

(1) Elder, *J. Am. Chem. Soc.*, **51** (1929), 3266.
(2) Buchböck, *Z. physik. Chem.*, **A, 156** (1931), 232.
(3) Kahler and DeEds, *J. Am. Chem. Soc.*, **53** (1931), 2998.
(4) Haugaard, *Chem. Abstracts*, **31** (1937), 930; *Kem. Maanedsblad*, **17** (1936), 33.
(5) Yoshimura, this Bulletin, **12** (1937), 359.

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On examining the data obtained, no correlation was found to exist between the asymmetry potential and the hydrogen electrode function of either side of the membrane, but there was a correlation between the asymmetry potential and the difference of $\Delta E/\Delta p\mathrm{H}$ of both surfaces, as shown in Fig. 1, where dots represent data referring to the MacInnes glass electrode, crosses those of the Morton glass electrode, and circles those of the commercial glass electrode. While these are data at 25°C., triangles represent those of commercial glass electrode determined at 18°C. The abscissa of Fig. 1 is the asymmetry potential in the solution of pH 3, e_3. The ordinate is the difference of the asymmetry potentials in the two solutions of pH 3 and pH 7, e_3-e_7, which is given by

$$e_3-e_7=\left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_o-\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_i\right\}\Delta p\mathrm{H} \qquad (1),$$

where ΔpH is the pH difference of the two solutions and is numerically 4. Suffixes i and o refer to the inner surface and the outer surface of the electrode membrane respectively. Thus the ordinate of the figure corresponds to the difference of $\Delta E/\Delta p\mathrm{H}$ between the two surfaces of the membrane as ΔpH is constant. The plots of all the electrodes made of the three mentioned sorts of glass tend to lie on the respective straight lines which pass near the origin with a slope of about 2. This indicates that the asymmetry potential approaches zero when the hydrogen electrode functions of both surfaces of the electrode membrane approach each other. This fact suggests in turn that the electromotive nature of the membrane surface which determines the hydrogen electrode function is correlated closely with that determining the potential level of the surface, because the asymmetry potential corresponds to the difference of the potential levels of the inner and the outer surfaces. Moreover, it is suggested that this relation differs according to the chemical composition of the glass, as correlation lines of the three sorts of glass differ from one another.

(2) The Relation between the Electromotive Effect and the Curvature of the Glass Membrane. It is seen in Fig. 1 that the hydrogen electrode function of the outer surface of an electrode membrane is in most cases lower than that of the inner surface and the asymmetry potential is negative, that is, the potential level on the inner side of the membrane is lower than that on the outer side. This difference of the electromotive effect of the outer and the inner surfaces of the electrode bulb is supposed to be due to the difference in the curvature of these

surfaces, and therefore to the strain or atomic arrangement of the surface layer. Elder[1] and also Buchböck[2] attempted to prove this supposition experimentally. The former failed in the experiment, while the latter succeeded. The present author also attempted to examine the problem. For the purpose, a bulb membrane of MacInnes glass electrode being fused into one end of a commercial glass tube, a MacInnes and Dole electrode of the diaphragm type was constructed. The convex surface of this electrode membrane is directed inside the electrode and the concave surface outside, while the relation is reverse in the electrode of bulb type. The asymmetry potential and the hydrogen electrode function of both the surfaces being estimated, data are plotted in Fig. 1 (designated with asterisks). The points tend to lie on the positive side of the correlation line of MacInnes glass electrode. It shows that the difference of the electromotive effect between the inner and the outer surfaces of the electrode membrane is caused by the difference of the curvature. This suggests that the electromotive effect of the glass membrane is closely related to the atomic arrangement of the surface layer[6]. Thus the asymmetry potential is supposed to be due to the difference of the atomic arrangement between the two surfaces of the electrode membrane.

(3) The Relation between the Electromotive Effect of the Glass Membrane and its Thickness. Kahler and DeEds[3] pointed out that the asymmetry potential of a glass electrode approaches zero as the thickness of the electrode membrane diminishes. This can be ascertained by the data given in Fig. 2, where the asymmetry potential (e_3 at 18°C. in most cases) of various electrodes of MacInnes glass (dots) and of commercial glass (circles) are plotted against the electrical resistance of the electrodes. The plots of the electrodes made of one and the same sort of glass tend to lie vaguely on a correlation line. Though the electrical resistance depends on the size of the electrode bulb besides the thickness of its membrane, it is principally determined by the latter, the size of the bulb depending also upon the thickness of the membrane, as the bulbs are blown on capillaries of about the same bore and the same thickness. Thus it can be maintained that a correlation exists between the thickness of the membrane and the asymmetry potential.

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(6) To prove this experimentally, the effect of annealing on the glass electrode potential was examined. Unfortunately, however, the effect of heat treatment of the electrode on its potential such as the effect or drying previously reported[7] covered the effect of annealing and the experiments ended in a failure. But the above suggestion as to the relation between the electromotive effect and the atomic arrangement cannot be denied on account of this failure.

This fact was ascertained further by the two following experiments: (i) A short MacInnes glass tubing of thick wall (which is about 0.4 mm. thick and serves as the electrode membrane) being connected with supports of commercial capillary tubing, an electrode of the type given in Fig. 1 in the previous report[5] was constructed. After its asymmetry potential and the hydrogen electrode function had been estimated on both the inner and the outer surfaces, the thick MacInnes glass tubing was blown to make a bulb of which the thickness of the thinnest part was 10 μ or so. The effect of this blowing on its potential was examined. See an example of the results given in Table 1. On making the membrane thinner, the asymmetry potential (in the absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces decreased.

Table 1. Effect of Blowing the Bulb.

Experiment	$\Delta E / \Delta p$H (mV./pH)			e_3 (mV.)	Thickness of the membrane (mm.)
	Inner surface	Outer surface	Difference		
Before blowing	58.3	47.8	10.5	−110.7	ca. 0.4
After blowing	58.2	58.1	0.1	−10.5	0.01

(ii) Either the inner or the outer surface of the thick membrane of the above-mentioned electrode being soaked in a concentrated HF for 1–2 hours, and thereafter in streaming water for several days, a thin lamella of the surface was stript off. The thickness of the membrane thus being reduced, the change in its electromotive effect was examined. Examples of data are given in Table 2. It was found in most cases that the hydrogen electrode function of the corroded surface approached that of the other surface of the membrane and the asymmetry potential decreased (in absolute value), while the reverse result was found in a few cases. As HF corrodes the glass surface ununiformly, the corroded surface may not be regarded as the same as that shaven mechanically. Deducing from the results of all experiments mentioned above, however, it is concluded that the asymmetry potential (in absolute value) and the difference of the hydrogen electrode function between the inner and the outer surfaces of the electrode membrane decrease simultaneously as the thickness of the membrane decreases.

Table 2. Effect of Hydrochloric Acid Treatment.

Experiment		$\Delta E/\Delta p$H (mV./pH)			e_3 (mV.)	Resistance (Ω)
		Inner surface	Outer surface	Difference		
I	Before treatment	58.0	47.6	10.4	−108.5	1.2×10^9
	After treatment	55.9	47.6	8.3	−89.5	1.0×10^9
II	Before treatment	57.9	52.8	5.1	−71.5	1.4×10^9
	After treatment	58.5	56.7	1.8	−23.5	1.2×10^9

I. The inner surface etched with HF.
II. The outer surface etched with HF.

The above-mentioned results cannot be explained by the deviation film theory of Kahler and DeEds[3] who maintained that the decrease of the thickness of the membrane is accompanied by increase of the hydrogen electrode function, for it is clear in Table 2 that the hydrogen electrode function on one surface has no direct correlation with the thickness of the electrode membrane. A plausible explanation is that the atomic arrangement of the inner and the outer surfaces of the membrane which are closely related with the factor determining both the hydrogen electrode function and the potential level of the surface tend to equalize with each other, as the thickness of the membrane decreases.

From data given in Table 2, it is also maintained that the glass membrane being regarded as an ensemble of many unit lamellæ, the electromotive effect of each lamella is different from the others. In the previous report[7], the same fact was maintained concerning assumed unit parts of the surface of the electrode membrane. This fact suggests that the atomic arrangement of the electrode membrane is different both lengthwise and breadthwise.

(4) Dependence of the Asymmetry Potential on the *p*H of the Solution and Discussion of the Above-Mentioned Results. From the above-mentioned experimental results, it is certain that the asymmetry potential is closely correlated with the difference of $\Delta E/\Delta p$H between the inner and the outer surfaces of the electrode membrane. This fact can be explained in either of the two following ways: (i) Experiments show that a linear relationship exists between the potential of the glass electrode and the *p*H of the solution at least in the range of *p*H 2–8, even when the hydrogen electrode function of the glass electrode is lower than

(7) Yoshimura, *J. Biochem.* (Japan), **21** (1935), 335.

the theoretical value. If this is correct not only roughly in the scope of experimental error, but also theoretically in the whole range of pH, the asymmetry potential e' in a solution of which the pH is higher by $\Delta p\mathrm{H}'$ than 3, is given by

$$e' = e_3 - \left\{\left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_o - \left(\frac{\Delta E}{\Delta p\mathrm{H}}\right)_i\right\}\Delta p\mathrm{H}' \qquad (2).$$

Thus the asymmetry potential of one and the same glass electrode is a linear function of pH. This equation has already been suggested by Kahler and DeEds[3]. If it is assumed in this equation that the asymmetry potential e' in a solution of a certain pH is kept constant among the electrodes made of one and the same sort of glass, a rectilinear relationship should exist between e_3 of the electrodes and the differences of $\Delta E/\Delta p\mathrm{H}$ between the inner and the outer surfaces of the electrode membranes. This certain pH should be ca. 11, as the slope of the correlation line experimentally found, i.e. $\Delta p\mathrm{H}'$, is ca. 2.

(ii) According to the current theories of the glass electrode, mentioned in the previous report[5], $\Delta E/\Delta p\mathrm{H}$ is given by

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left[1 - \frac{1}{\Delta p\mathrm{H}}\log\left\{\frac{\left(1+\frac{C'_{\mathrm{Na}}}{C'_{\mathrm{H}}}\frac{Y}{X}\right)^n}{\left(1+\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}\right)^n}\right\}\right] \qquad (3).$$

R' represents 2.303 R. C_{H} and C'_{H} are the hydrogen ion concentrations of the two buffer solutions used for the determination of $\Delta E/\Delta p\mathrm{H}$, and C_{Na} and C'_{Na} their sodium ion concentrations, the cation of the salt being assumed to be sodium ion. $\Delta p\mathrm{H}$ is equal to $\log C_{\mathrm{H}}/C'_{\mathrm{H}}$. As to the constants n, X and Y, see the previous report. When the hydrogen ion concentration C_{H} is sufficiently high, the term $\frac{C_{\mathrm{Na}}}{C_{\mathrm{H}}}\frac{Y}{X}$ can be neglected, and we have

$$\frac{\Delta E}{\Delta p\mathrm{H}} = \frac{R'T}{F}\left[1 - \log\left(1+\frac{C'_{\mathrm{Na}}}{C'_{\mathrm{H}}}\frac{Y}{X}\right)^n \Big/ \Delta p\mathrm{H}\right] \qquad (4).$$

This is the equation of $\Delta E/\Delta p\mathrm{H}$ given in the previous report[8]. From this equation, it is clear that $\Delta E/\Delta p\mathrm{H}$ is not a constant but a function of pH and the salt concentration when $\Delta E/\Delta p\mathrm{H}$ is smaller than the

(8) The derivation of this equation is given here as an addendum to the previous report[5].

theoretical value $R'T/F$. Thus equation (2) is not valid theoretically, and the asymmetry potential e_g is given by

$$e_g = \frac{R'T}{F} \log \left\{ \frac{1+\frac{C_{Na}}{C_H}\frac{Y_o}{X_o}}{1+\frac{C_{Na}}{C_H}\frac{Y_i}{X_i}} \right\}^n + \frac{R'T}{F} \log \frac{X_o}{X_i} \qquad (5),$$

which is equal to equation (2) given in the previous report. Suffixes i and o refer to the inner and the outer surfaces of the electrode membrane respectively. When C_H is sufficiently large, we have

$$e_g = \frac{R'T}{F} \log \frac{X_o}{X_i} \qquad (6).$$

From equations (4) and (6), it is clear that, when the constant X decreases on one surface of the membrane as compared with that on the other surface, the potential level of that surface rises against that of the other surface, causing the change in the asymmetry potential, and the hydrogen electrode function on that surface decreases. Thus the fact found in the present experiments can be explained by the current theories of the glass electrode.

Now it should be decided which of explanations (i) and (ii) is correct. For this purpose, equations (2) and (5) were examined experimentally, of which the former indicates that the asymmetry potential is a linear function of the pH of the solution, while the latter indicates that the function is a curve which tends to transit into a plateau in the range of low pH, as C_{Na}/C_H decreases.

Measuring the asymmetry potential of one and the same electrode in various buffer solutions of different pH but of 0.1 molar sodium ion concentration, data were plotted against the pH, of which examples obtained on a MacInnes glass electrode (dots) as well as a commercial glass electrode (circles) is given in Fig. 3. Plots did not lie on a straight line, but on a curve which showed that the asymmetry potential (not in absolute value) decreases with the decrease in pH but tends to attain a constant value in the range of low pH. Thus explanation (ii), but not (i), is to be adopted.

The above-mentioned theoretical correlation between the asymmetry potential and the difference of hydrogen electrode functions of both surfaces of the electrode membrane can be verified quantitatively to a certain extent as follows:

Putting $$\delta \equiv \frac{R'T}{F} \log\left(1+\frac{C_{Na}}{C_H}\frac{Y}{X}\right)^n,$$

we have

$$\log\left\{\frac{\text{Antilog}\dfrac{\delta_i}{\frac{nR'T}{F}}-1}{\text{Antilog}\dfrac{\delta_o}{\frac{nR'T}{F}}-1}\right\} = \text{const.}+\log\frac{X_o}{X_i} \qquad (7),$$

the suffixes o and i referring to the outer and the inner surfaces of the membrane respectively. From equation (4),

$$\delta = \frac{R'T}{F}\Delta p\mathrm{H}-\Delta E \qquad (8),$$

and from equation (6),

$$\log\frac{X_o}{X_i} = \frac{e_3}{\frac{R'T}{F}} \qquad (9),$$

assuming that the cation effect on the asymmetry potential is negligible in the range near pH 3. Thus equation (7) was quantitatively examined, calculating δ and $\log(X_o/X_i)$ by equations (8) and (9) from the experimental data obtained in section (1). The result is given in Fig. 4, where n in the equation (7) is taken as 1/2 according to Gross and Halpern[9]. The plots lie vaguely between two parallel boundary lines of which the slope is 1. The reason why the plots do not lie on a straight line, but scattered in a zone is probably that the "const." in equation (7) is not the same among different electrodes, and moreover the assumptions made in this examination may not be completely correct. Thus it can be stated that equation (7) was verified somewhat quantitatively. Even when n is taken as 1 according to Dole[9] and Horovitz[9], the same result is obtainable. Therefore the decisive criticism of the three current theories cited in the previous report can not be deduced from the present experimental results. Moreover, it would be premature to accept any one of the current theories as completely correct only from the present experimental results.

It is interesting, however, to try to explain the experimental facts by the current theories. It was found in the above-mentioned experiments

(9) See the discussion in the previous report[5].

that the hydrogen electrode function of the outer surface is lower than that of the inner surface and the potential level of the former which determines the asymmetry potential is higher than that of the latter. The explanation given for the fact is that the constant X in equations (4) and (6) on the outer surface is smaller than that on the inner surface. The physical meaning of this explanations is that the energy

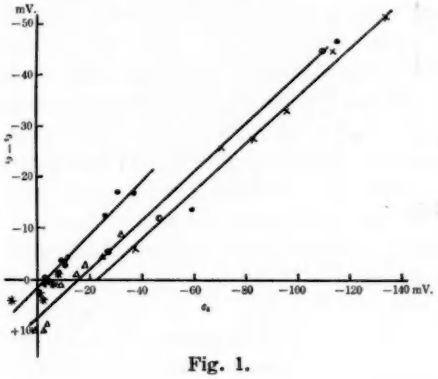

Fig. 1.

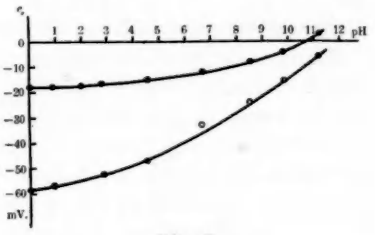

Fig. 3.

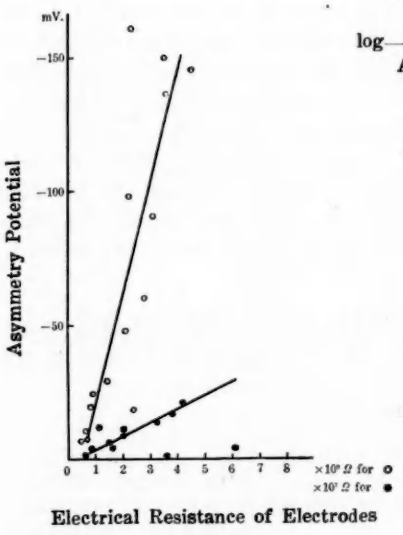

Fig. 2.

$$\log \frac{\text{Antilog} \dfrac{\varepsilon_i}{\frac{R'T}{2F}} - 1}{\text{Antilog} \dfrac{\varepsilon_o}{\frac{R'T}{2F}} - 1}$$

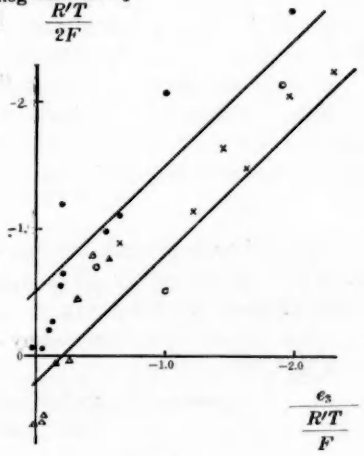

Fig. 4.

of hydrogen ion on the lowest quantum level of the glass phase according to Dole[9] is greater on the convex surface than that on the concave surface, probably owing to the difference of the atomic arrangements of these surfaces. To elucidate further the interrelation between the constants in the above-mentioned theoretical equation and the atomic arrangement of the surface is a problem left for future study.

Conclusions. (1) When the difference between the hydrogen electrode functions of the inner and the outer surfaces of a glass membrane is large, a high asymmetry potential appears, and the hydrogen electrode function on the positive side of the asymmetry potential is in most cases smaller than that on the other side. Thus a correlation exists between the difference of the hydrogen electrode functions of the two surfaces and the asymmetry potential. This indicates that an intimate relationship exists between the factor which determines the potential level of the surface referring to the asymmetry potential, and that of the hydrogen electrode function. This fact can be explained qualitatively by the current theories of glass electrode.

(2) The hydrogen electrode function is, in most cases, less on the convex surface than on the concave surface of an electrode membrane, and the positive pole of the asymmetry potential is, in most cases, on the convex side. This difference between the hydrogen electrode functions of both surfaces and also the magnitude of the asymmetry potential tend to decrease as the thickness of the electrode membrane diminishes. These facts suggest that the electromotive effect of the surface of a glass membrane is closely connected with the atomic arrangement between the inner and the outer surfaces of the electrode membrane.

A glass membrane being regarded as an ensemble of many lamellæ and unit surfaces, the electromotive effects of these parts are different from one another. Therefore, the atomic arrangement of the glass membrane is probably different in each part both lengthwise and breadthwise.

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Über eine hochungesättigte Fettsäure $C_{24}H_{38}O_2$ aus dem Öle des Thunfisches, *Tynnus tynnus* L.

Von Sei-ichi UENO und Shin-ichiro TAKASE.

(Eingegangen am 22. September 1937.)

Über hochungesättigte Fettsäuren der C_{24}-Reihe aus Fischölen sind von mehreren Autoren Untersuchungen angestellt worden. H. Bull[1] fand eine Säure $C_{24}H_{40}O_2$ im Heringsöle. S. Ueno und M. Iwai[2] erhielten Scoliodonsäure $C_{24}H_{38}O_2$ aus dem Lebertran von „Hiragashira", *Scoliodon laticaudus* Müller und Henle. Y. Toyama und T. Tsuchiya[3] beschrieben das Vorkommen von $C_{24}H_{36}O_2$, $C_{24}H_{38}O_2$ und $C_{24}H_{40}O_2$ in Sardinenöle und die Konstitution der Nisinsäure $C_{24}H_{36}O_2$. S. Ueno und C. Yonese[4] konnten aus dem Öle des Thunfisches eine Säure $C_{24}H_{38}O_2$ isolieren, der vermutlich eine Säure $C_{24}H_{36}O_2$ beigemischt sein dürfte.

In der vorliegenden Arbeit haben wir den Ozonabbau der aus dem Thunfischöle gewonnenen Säure $C_{24}H_{38}O_2$ studiert, um die Konstitution dieser Säure aufzuklären. Im Abbauprodukt des Ozonides konnten wir Acetaldehyd, Propionaldehyd, Kohlendioxyd und Bernsteinsäure feststellen. Daraus lässt sich ableiten, dass sich folgende Atomgruppen in der Säure $C_{24}H_{38}O_2$ befinden: CH_3-CH_2-CH=, =CH-CH_2-CH= bzw. =CH-CH_2-COOH, =CH-CH_2-CH_2-CH= bzw. =CH-CH_2-CH_2-COOH. Kohlendioxyd und Acetaldehyd sind möglicherweise sekundäre Abbauprodukte von Malonaldehydsäure, die aus dem Gruppenteile =CH-CH_2-CH= od. =CH-CH_2-COOH entstehen mag. Eine eingehendere Untersuchung konnten wir wegen Mangels an Material noch nicht ausführen.

Beschreibung der Versuche.

Die hochungesättigte Säure, welche der Formel $C_{24}H_{38}O_2$ entspricht, war ein Nebenprodukt bei der Untersuchung der gesättigten Fettsäuren im Thunfischöle; darüber haben S. Ueno und C. Yonese in Nippon Kwagaku Kwaishi (japanisch) berichtet. Die Eigenschaften des Thunfischöles waren: d_4^{20} 0.9264; n_D^{20} 1.4820; J.Z. (Wijs) 190.1; S.Z. 4.2; V.Z. 183.4. Die aus dem obigen Öle (3 kg.) gewonnenen

(1) H. Bull, *Chem.-Ztg.*, **23** (1899), 996.

(2) S. Ueno und M. Iwai, *J. Soc. Chem. Ind., Japan*, **37** (1934), 251.

(3) Y. Toyama und T. Tsuchiya, *J. Soc. Chem. Ind., Japan*, **37** (1934), 530; dieses Bulletin, **10** (1935), 543, 547.

(4) S. Ueno und C. Yonese, dieses Bulletin, **11** (1936), 440.

Methylester der Fettsäuren wurden fraktioniert und die über 200°/3 mm. siedende Fraktion wurde noch zweimal der fraktionierten Destillation unterworfen. Die Resultate der letzten Destillation waren wie folgt.

Nr.	Siedept. (°C./3 mm.)	Ausbeute (g.)	n_D^{20}
1	-200	3.0	1.4815
2	200-205	6 0	
3	205-209	29.0	1.4840
4	209-210	64.5	1.4850
5	210-220	41.0	1.4870
6	220-224	51.0	1.4880
7	224-226	46.0	1.4875
8	226-	15.0	1.4885
9	Rückstand		

Die Trennung und der Ozonabbau der hochungesättigten Säure $C_{24}H_{38}O_2$. Die aus der Fr.Nr.7 gewonnene Fettsäure wurde mit Hilfe der Bleisalz-Alkohol-Methode und Natriumsalz-Aceton-Methode weiter gereinigt. So ergaben sich zum Schluss 6 g. hochungesättigte Fettsäure mit folgenden Eigenschaften: N.Z. 154.0; J.Z. (Wijs) 342.9; n_D^{20} 1.5075. Der Bromgehalt des ätherunlöslichen Polybromides war 67.7%. (Ber. für $C_{24}H_{38}O_2$: N.Z. 156.6; J.Z. 354.2. Ber. für $C_{24}H_{38}O_2Br_{10}$: Br, 69.05%). Die hochungesättigte Fettsäure (3.85 g.) wurde in 50 c.c. Chloroform gelöst und unter Kühlung mit einer Kältemischung ca. 7%iges Ozon 4 Stunden lang eingeleitet. Bei der Abdestillation des Lösungsmittels unter vermindertem Druck blieben 5.2 g. eines gelben harzigen Ozonides zurück. Das Ozonid wurde mit 50 c.c. Wasser unter Rückfluss auf dem siedenden Wasserbad im Wasserstoffstrom erhitzt. Die entwickelten Gase wurden in 50 c.c. kaltem Wasser, dann in 300 c.c. und schliesslich noch in 200 c.c. Barytwasser (ca. N/3) absorbiert.

Nachweis des Acetaldehyds und des Propionaldehyds. Die wässrige Lösung des flüchtigen Zersetzungsprodukts hatte einen angenehmen Geruch und gab die Schiffsche Reaktion; mit Natriumnitroprussid und Kalilauge färbte sie sich rot; mit Piperidin und Natriumnitroprussid blau; mit *m*-Phenylendiamin-Salzsäure Lösung zeigte sie grüne Fluorescenz. Beim Versetzen mit einer Lösung von *p*-Nitrophenylhydrazin schieden sich gelbe nadelförmige Kristalle aus, welche nachdem sie aus Toluol und verdünntem Alkohol umkristallisiert wurden, bei 117.5–119° schmolzen. Dieser Schmelzpunkt ist sowohl niedriger als der des Acetaldehyd-*p*-nitrophenylhydrazons (Schmp. 128°), als auch des Propionaldehyd-*p*-nitrophenylhydrazons (Schmp. 124°), aber eine Mischung von den gelben nadelförmigen Kristallen mit Propionaldehyd-*p*-nitrophenylhydrazon (Schmp. 123–124°), das aus Kahlbaumschem Propionaldehyd hergestellt wurde, schmolz bei 119.5–121° (Gef.: N, 22.48. Ber. für $C_9H_{11}O_2N_3$: N, 21.76; Ber. für $C_8H_9O_2N_3$: N, 23.46%). Aus den Analysenwerten könnte man unter Berücksichtigung der oben beschriebenen Farbenreaktionen schliessen, dass die gelben Kristalle eine Mischung von Acetaldehyd- und Propionaldehyd-*p*-nitrophenylhydrazon sind.

Kohlendioxyd. In der Baryt-Lösung entstand ein weisser Niederschlag von Bariumcarbonat (1.6 g.), woraus das entstandene Kohlendioxyd berechnet wurde (Gef.: CO_2, 9.4%). Kohlendioxyd ist ein sekundäres Zersetzungsprodukt der Malonsäure od. ihres Halbaldehyds; die vollkommene Abspaltung von Kohlendioxyd aus einer Atomgruppe $=CH\text{-}CH_2\text{-}CH=$ od. $=CH\text{-}CH_2\text{-}COOH$ in $C_{24}H_{38}O_2$ müsste 12.3% betragen.

Bernsteinsäure. Die wässrige Lösung der nichtflüchtigen Zersetzungsprodukte wurde von der harzigen Substanzen getrennt. Ein Teil der Lösung wurde mit Ammoniak versetzt, konzentriert und der Zinkstaubdestillation unterworfen. Der entstehende Dampf färbte einen mit Salzsäure befeuchten Holzspan rot. Auf Grund dieser charakteristischen Farbenreaktion des Pyrrols kann man auf das Vorhandensein von Bernsteinsäure in der wässrigen Lösung schliessen. Den Ätherextrakt der wässrigen Lösung haben wir mit Kaliumpermanganat oxydiert und konnten aus dem Oxydationsprodukt weisse Kristalle erhalten, die, nachdem sie aus Essigäther umkristallisiert wurden, bei 182° schmolzen. Die Mischprobe mit einem reinen Präparat der Bernsteinsäure (Schmp. 183–184°) zeigte keine Depression des Schmelzpunktes.

Über die harzigen Substanzen haben wir keine genauere Untersuchung gemacht, sondern lediglich festgestellt, dass es nicht gelingt eine höhere Dicarbonsäure als Bernsteinsäure daraus zu isolieren. Wir wollen mit einer grösseren Menge Material weitere Untersuchungen ausführen.

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Studies on Fluorine at Low Temperatures. III. Dissolution of Chlorine in Liquid Fluorine.

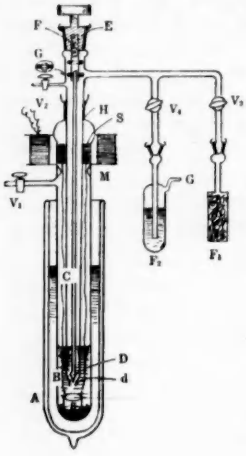
By Shin-ichi AOYAMA and Eizo KANDA.

(Received August 12th, 1937.)

Merck's potassium bifluoride contains 0.17% chlorine. When it is electrolysed, chlorine of the chloride in the molten salt is expelled by fluorine and the produced fluorine gas is contaminated with chlorine gas, and sometimes traces of chlorine can be found in liquid fluorine. Of course, such occurs only while the salt is fresh, and no chlorine exists in the salt which has been subjected to electrolysis for a long time.

It is unusual that a solution of crystals exists at such a low temperature as that of liquid fluorine. The present authors carried out measurements as to this interesting case.

I. Apparatus. A special apparatus as shown in the accompanying figure was devised for the purpose of taking a sample for analysis, and used in the analysis of liquid air and a solution of chlorine in liquid fluorine. A is a Dewar vessel to keep liquid nitrogen, B a glass pipe 30 mm. in diameter, where fluorine entering at V_2 is condensed, C a Pyrex glass sampler for the solution, 10 mm. in diameter, D a valve spindle made of Pyrex glass, the top of which is connected with the lower end of the copper rod. F has a screw-thread cut on it and the spindle goes up and down as cap E in the upper part with ground glass surface is turned, and thus the ground glass surface joint between D and d at the lower end is opened or closed. Two copper pieces are attached to the lower part of F as shown in the figure. The cross-section of the pipe at this point is made elliptical (G), so that F does not rotate but only goes up and down when E rotates. S is a stirrer, M an electric magnet for working the stirrer S, F_1 a silver-plated copper vessel filled with many small coils of silver filament and acts as an absorber of fluorine, and F_2 a glass vessel in which an aqueous solution of silver nitrate is placed to absorb fluorine and chlorine.



II. Operation. Fluorine or chlorine is introduced at V_2. V_1 is an opening for evacuating the apparatus in advance. The interior of F_1 is also previously evacuated. When a proper amount of solution is condensed on the bottom of B, the stirrer S is moved up and down by operating M and the liquid is made homogeneous. The valve D is closed by turning E and the sample of liquid is accumulated in C.

By turning H, B and C are disconnected at the ground glass surface junction. C is drawn up slightly from the liquid fluorine and the solution is gradually vaporized. When V_3 is opened and F_1 is heated to 200°C., the sample in C is vaporized and the fluorine, acting on the silver, is absorbed. Care must be taken so that sudden boiling may not take place at the time of vaporization and the crystals of the segregated solute and a small quantity of the solution may finally remain. Then V_3 is closed and V_4 is opened. In this way the remainder of fluorine and the crystals of the segregated chlorine are vaporized and the vapour produced is passed through the solution of silver nitrate in F_2.

The solution of silver nitrate is first made ammoniacal, and is acidified with nitric acid after the halogens have been passed through it. To make ammoniacal is intended for preventing a part of chlorine from becoming soluble $AgClO_3$.

The gas in C is drawn by working a pump at G and by introducing air at V_2. All the gas in C is passed through F_2.

III. Quantitative determination of fluorine and chlorine. (1) The greater part of fluorine, apart from chlorine, is acted on by the silver filament in F_1, and makes silver fluoride. The quantity of fluorine is determined by weighing F_1.

(2) The solution of silver nitrate, the deposits of silver fluoride and silver chloride are carefully poured from F_2 into a bakelite beaker and are acidified with nitric acid, whereby the silver fluoride is dissolved. Then the solution is filtered and the residue of silver chloride is weighed. Thus, the quantity of chlorine can separately be determined.

(3) The filtrate contains silver fluoride and silver nitrate. With an addition of aqueous solution of NaCl, it is precipitated as silver chloride. Then by removing the deposit a filtrate of NaF can be obtained. This filtrate is made alkaline by adding an aqueous solution of Na_2CO_3 to it. Then deposits of $CaCO_3$ and CaF_2 are formed by adding a solution of $CaCl_2$ to this alkaline filtrate. When $CaCO_3$ alone is dissolved by acetic acid, CaF_2 remains as deposit. This deposit is filtered and weighed, and the quantity of fluorine is determined from CaF_2.

IV. Results of measurements. (1) Fluorine obtained from a new electrolyte of potassium bifluoride. Fluorine as AgF in F_1 1.0524 g., as CaF_2 in F_2 0.1155 g., total 1.1679 g. Chlorine as AgCl in F_2 0.0075 g. Thus, the percentage of chlorine in the mixture was found 0.64.

(2) The percentage of chlorine in fluorine produced from an old electrolytic salt was 0.09%.

(3) Quantity of chlorine in liquid fluorine saturated at −195°C. Chlorine was separately introduced, condensed, and precipitated. After stirring, the solution was analysed with the result as follows: Fluorine as AgF in F_1 0.7145 g., as CaF_2 in F_2 0.1227 g. Chlorine as AgCl in F_2 0.0088 g. The quantity of chlorine in the solution saturated at −195°C. was 1.04%.

The authors express their hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

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Studies on Fluorine at Low Temperatures. IV. Separation of Fluorine from Oxygen by Adsorption and Rectification.

By Eizo KANDA.

(Received August 12th, 1937.)

As was stated in the first paper, fluorine is often contaminated with oxygen, the boiling points, −188°C. and −183°C. respectively, being rather close. Removal of oxygen from fluorine with chemical reagents would be practically impossible, because fluorine acts upon almost all substances at ordinary temperature. Besides, it is desired to handle fluorine at low temperatures to avoid its chemical activity. Therefore, the author examined the possibility of separation of fluorine from oxygen by adsorption upon charcoal at low temperatures.

Experiments on separation were also made by means of a rectification still, because the difference between the boiling points is as small as 5°, and accordingly the separation by fractional distillation of the liquid might be very difficult.

I. Experiment on Adsorption. (1) *Apparatus.* The ordinary method of determining the adsorption of gases, in which the sample of the adsorbent (for instance, charcoal) is placed in a glass or quartz vessel and the variation of the volume or pressure of the gas due to adsorption is determined by reading the mercury column, was not applicable in this case, because glass, quartz and mercury are attacked by fluorine. The author, therefore, used the method with a spring balance for reducing the error.

In Fig. 1, A is a trap in which pure liquid fluorine is kept and which is cooled by liquid nitrogen. In the trap is a heating coil H. The fluorine is vaporized in a desired quantity and the vapour is carried into B. B has a spring balance in it, and at the end of the balance a platinum-plated quartz scale is hung by a platinum filament. T is a thermocouple made of copper and constantan wires, which is placed near the test piece for determining the temperature. An outline of the apparatus for obtaining desired low temperatures is represented by two Dewar vessels, which are similar to one used by the author for calibrating thermocouples by means of a hydrogen thermometer[1].

(1) Aoyama and Kanda, this Bulletin, **10** (1935), 472.

Spring balance. A quartz thread 0.4 mm. in diameter was wound in the form of a spring having a diameter of about 15 mm., the number of turns being 60 and the sensitivity 25 mm./0.1 g. The platinum-filament was fitted with the scale at its lower end in advance, and platinum weights of 0.1 g., 0.2 g.,.... 2 g. were placed on the scale. The elongation of the spring was determined by a cathetometer and was calibrated against the weights. As illustrated, the upper end of the spring was connected to a platinum thread, which was wound round a cock placed on the top of B, and the scale was brought into a proper position by turning the cock. Otherwise, the temperature of the test piece would have varied with the movement of the scale, which must take place as the result of expansion

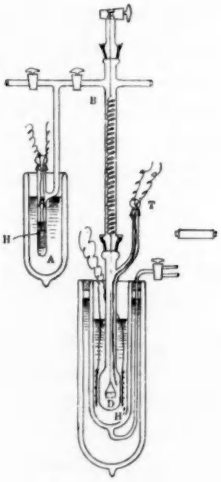

Fig. 1.

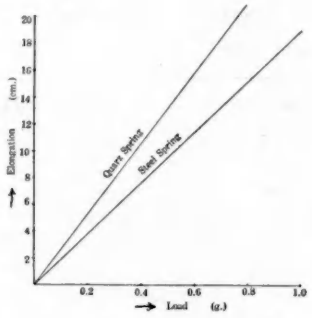

Fig. 2.

and contraction of the spring due to variation of the weight of the test piece during the experiment. The quartz thread was covered with platinum film for fear of its being destroyed by fluorine. A steel spring (0.2 mm.) was also used. The weights were examined before and after each experiment. An example of the results of experiments is given in Fig. 2.

(2) *Adsorption of oxygen gas.* The adsorption of oxygen gas was determined at −160°, −100°, −40°C. and at the pressures of 600, 400, 350, and 200 mm. As for the adsorbent, cocoanut-charcoal was baked at 700°C., activated with oxygen, and made vacuous while it was being baked.

The adsorption for 1 g. of charcoal as expressed in c.c. at N.T.P. was shown in Table 1. This result, together with the adsorption of fluorine, is illustrated in Fig. 4.

(3) *Adsorption of fluorine gas.* Similar experiments were made with fluorine. The progress of adsorption with the lapse of time is given in Fig. 3. The time required for saturation was about 3 hours.

Table 1.

Temp. (°C.) / Press. (mm.)	−160	−100	−40	0
760	136	50	32	10
600	123	44	26	—
400	104	30	20	—
200	80	18	—	—

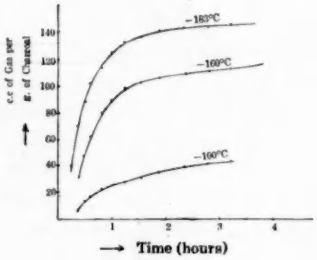

Fig. 3.

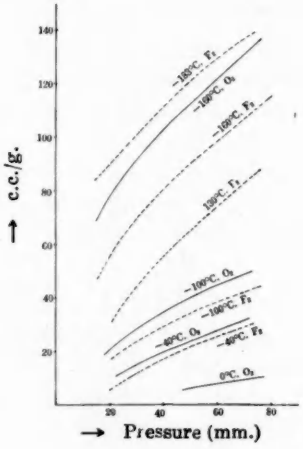

Fig. 4.

The amounts of adsorption in the saturated state are given in Table 2. Fluorine gas was introduced slowly after the charcoal had attained the temperature of the cooling vessel lest it should act upon charcoal. Further, the spring balance was examined several times.

The author expected that fluorine would be adsorbed in a greater quantity than oxygen because of its chemical reactivity against charcoal at ordinary temperature, but the reverse was the case. Oxygen was adsorbed in a greater quantity than fluorine at every temperature. The difference of the amounts of adsorption between them became greater with the fall of temperature. After a mixture of 96% fluorine and 3.7%

Table 2.

Press. (mm.) \ Temp. (°C.)	−183	−160	−100	−40	0
760	142	111	44	30	13
600	128	98	40	24	—
400	109	80	30	16	—
200	86	60	17	—	—

oxygen was adsorbed upon the charcoal at −180°C., the remaining gas contained 97% fluorine and 2.8% oxygen. After the same operation was repeated 5 times, the gas was refined up to 99.4% fluorine and 0.4% oxygen. Adsorption, therefore, may be used for refining fluorine.

II. Experiment on Rectification. A rectifier made of Pyrex glass and filled with glass beads was used for the experiment (Fig. 5). V_1 and V_2 are Dewar vessels, and the inside of V_1 forms the rectifying tower. A heating coil H is placed on the bottom, and a mixed liquid of fluorine and oxygen is vaporized in it. The still is 80 cm. long, and is filled with glass beads 5 mm. in diameter. The top of the still has a glass tube C inserted, and is made air-tight with plaster. Liquid air is poured into C from another Dewar vessel, V_3. The temperature of the liquid air in C is controlled by varying its composition and serves as a condenser. A part of the vapour rising in the still is condensed by this condenser, and

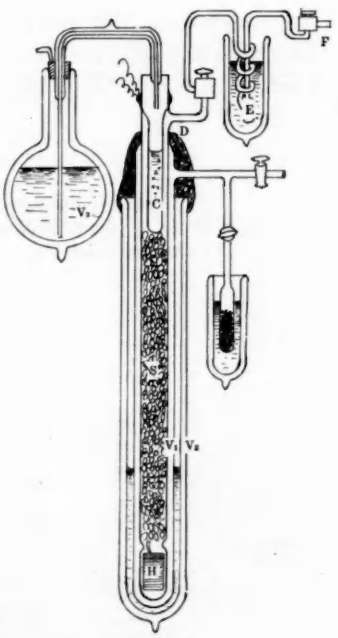

Fig. 5.

the vapour which has become fluorine-rich goes through D and is condensed in the trap E which has been cooled by liquid nitrogen: The substance which has been collected in E is taken out through F, and then subjected to the analysis of fluorine using mercury.

The vaporizer, still, and condenser are fitted with thermocouples for observing the temperature. Dewar vessel V_2, the gas-introducing tube attached on the outside of the Dewar vessel V_1, and the charcoal trap serve for cooling the rectifying tower and keeping it at a proper temperature. By using this refining apparatus, 99% pure fluorine could be obtained in E from an original liquid containing 95% fluorine.

In short, purification of fluorine must always be done at a low temperature, but the purest fluorine that can be obtained by the rectifying process is 99%, and therefore a percentage higher than this can be reached only by means of adsorption.

In conclusion, the author expresses his cordial thanks to Prof. Aoyama who advised him through this work. The author also expresses his hearty thanks to the Japan Society for the Promotion of Scientific Research for a grant.

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Studies on Fluorine at Low Temperatures. V. Viscosity of Fluorine Gas at Low Temperatures.

By Eizo KANDA.

(Received August 12th, 1937.)

Determination of the size, mean free path, and mean velocity of fluorine molecule, though important in the study of the reaction of fluorine gas, has not yet been made. The present author is now making a study of the reaction velocity of fluorine gas. But prior to this, he determined the viscosity of fluorine, and deduced the above-mentioned constants from it.

I. Method and Apparatus. For the determination of viscosity, two methods are available: observation of flow in a capillary tube and that of oscillation-rotation of a disc. In the author's measurements with fluorine, (i) the apparatus had to be as compact as possible for ensuring a constant low temperature, and (ii) mercury could not be used because of the corrosive nature of the gas. For this reason, the author adopted the second method in which decrement of the oscillation-rotation of the disc was measured.

H. Vogel's apparatus[1] was remodelled in some measure. The author's apparatus is illustrated in Fig. 1, where A, B, and C are made of hard glass and they are connected by ground junctions S_1 and S_2. C has a glass cock S_3, around which a platinum filament is wound. The filament is moved upward and downward by turning the cock. B has a window W, and A is fitted with a branch tube D for introducing fluorine and with a device of the oscillating disc E. E, as separately illustrated in details, consists of a, b, and c, where b is the oscillatory rotating disc and is hung from S_3 with a nickel wire N and a platinum wire P, thus lying at equal distances from a and c. Further, a, b, and c are made of nickel-plated brass, and E is set in contact with c on the ground glass

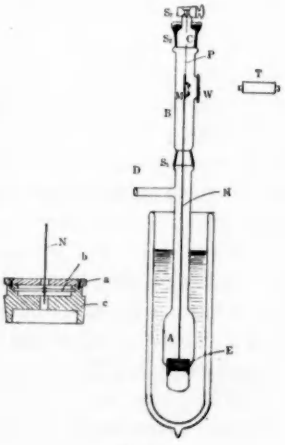

Fig. 1.

(1) Vogel, *Ann. Physik*, **43** (1914), 1235.

surfaces. In B, as illustrated, is a mirror M, whose oscillation-rotation is observed by means of a telescope through W at a distance of 2 metres. The dimensions of the important parts of E are as follows: diameter of the oscillating disc 30 mm., thickness 1.8 mm., weight 10.8 g., weight of the suspended parts 13.1 g., distance of surfaces between a and b or b and c 1.2 mm., and period of oscillation about 10 sec.

The device for winding up the platinum wire lowers the disc when the experiment has been finished or puts the disc in a proper position between a and c when the experiment is about to be made. On being slightly revolved, S_2 gives a moment of revolution to the disc.

Apparatus for maintaining a low temperature and for measuring the temperature are represented in a simple way by Dewar vessels. In practice, however, a thermostat was used, which had been often used in the author's experiments at low temperatures. The temperature was determined by means of a thermocouple made of copper and constantan.

II. Determination of the Viscosity. From the ratio of damping of the oscillation of the revolving disc, the viscosity can be determined by the following equation:

$$\eta = \frac{\lambda - K}{\tau c} \qquad (1),$$

where η is viscosity, τ period of oscillation, λ logarithmic decrement of oscillation, K a part of λ, that is, logarithmic decrement due to friction of the parts other than the disc, and c a constant peculiar to the apparatus.

λ and τ in the foregoing equation are obtained by observation using the mirror, scale, and stop-watch. It will be seen that c can be eliminated by the method described below. K is determined by the following somewhat complicated process.

K consists of (i) decrement due to the torsion of the platinum wire, K_1, and (ii) decrement due to friction between the gas and the mirror and other parts, K_2. Namely, $K=K_1+K_2$. K_1 depends upon the tension of the platinum wire and K_2 upon the kind and pressure of gas. In the case of vacuum, $K_2=0$.

When the material and weight of the disc are varied, with its geometrical dimensions being kept unvaried, $K'=K_1'+K_2$.

Since the period of the oscillation, τ, is independent of the temperature nor the kind of gas, but depends upon the apparatus alone, we may put $c\tau=C$.

As, in the case of vacuum, the total decrement λ which is obtained by observation is K_1, K_1 is a magnitude which can be determined by

observation. In the case of the author's experiment, $K_1=0.00031$, and $K_1'=0.00034$.

In the case of air, if the viscosity at 0°C. and T are represented by η_0 and η_T respectively, we shall have, from equation (1),

$$C\eta_0 = \lambda-(K_1+K_2) \quad (2), \qquad C'\eta_0 = \lambda'-(K_1'+K_2) \quad (3),$$
$$\eta_0(C-C') = (\lambda-K_1)-(\lambda'-K_1') \quad (4).$$

Similarly,

$$C\eta_T = \lambda_T-(K_1+K_2) \quad (5), \qquad C'\eta_T = \lambda_T'-(K_1'+K_2) \quad (6),$$
$$\eta_T(C-C') = (\lambda_T-K_1)-(\lambda_T'-K_1') \quad (7).$$

From (4) and (7)

$$\frac{\eta_0}{\eta_T} = \frac{(\lambda-K_1)-(\lambda'-K_1')}{(\lambda_T-K_1)-(\lambda_T'-K_1')} \qquad (8).$$

In equation (7), K_2 is eliminated, and the terms on the right side are magnitudes each of which can be determined by observation.

If η_0 is given, η_T will be obtained from the foregoing equation.

From (2) and (5), we have

$$\frac{\eta_0}{\eta_T} = \frac{\lambda-(K_1+K_2)}{\lambda_T-(K_1+K_2)} \qquad (9).$$

From this equation, we get

$$K_2 = \frac{\eta_0(\lambda_T-K_1)-\eta_T(\lambda-K_1)}{\eta_0-\eta_T} \qquad (10).$$

Thus K_2 is finally determined. K_2 is proportional to the square root of the viscosity of gas, that is,

$$K_2 \propto \sqrt{\frac{\eta}{\eta_0}} \qquad (11).$$

With the author's apparatus, the decrement obtained in vacuum was $K_1=0.00031$. As to air, K_2 obtained from equation (10) was $K_2=0.00010$. Hence,

$$K = K_1+K_2 = \left(31+10\sqrt{\frac{\eta}{\eta_0}}\right)\times 10^{-5}.$$

If we use λ_0 and K_0 for the logarithmic decrement of air at 0°C., and λ and K for any other gas, with a given apparatus at a given temperature, we shall have

$$\eta = \eta_0 \frac{\lambda - K}{\lambda_0 - K_0} \tag{12}$$

Thus, if the viscosity of air at 0°C. is given, η of any other gas can be deduced from it.

Further, in equation (11), the ratio of λ can stand for the ratio of viscosity. Thus, $K_2 \infty \sqrt{\frac{\lambda}{\lambda_0}}$.

III. Determination of the Logarithmic Decrement. Let the reading of a certain leftward movement of the mirror in the course of oscillatory rotation be represented by a and the succeeding rightward movement by b, then $a/b=n$, $\lambda=\log n$.

In practice, the mirror is vibrated several times, and its deflection is observed. The following relation exists:

$$\frac{a_\nu + b_{\nu+1}}{a_{\nu+15} + b_{\nu+16}} = n^{30}, \quad \lambda = \log n = \frac{1}{30} \log \frac{a_\nu + b_{\nu+1}}{a_{\nu+15} + b_{\nu+16}}.$$

IV. Results of Measurement. (1) *Air.* The observed values of decrement of oscillation are given in Table 1.

Table 1.

$a_\nu + b_{\nu+1}$	$\log (a_\nu + b_{\nu+1})$	30λ
53.79	1.73070	
43.54	1.63889	
35.49	1.55011	
28.83	1.45984	
23.40	1.36920	
19.03	1.27944	0.45126
15.44	1.18893	0.44998
12.55	1.09864	0.45147
		Average 0.45090

$\lambda_0=1/30$ (0.45090) $=0.015030$.

Further, $\tau=11.20$ sec., $\lambda_0-K_0=0.015030-0.00041=0.014620$.

(2) *Hydrogen.* To check the above-mentioned method and apparatus, determination was made with hydrogen gas at various low tem-

peratures. The hydrogen was obtained by electrolysis of water and refined by means of palladium catalyser. The results are given in Table 2.

Table 2.

t	T	p	λ	K	$\eta\times10^5$
0	273.2	764	0.007639	0.00038	856
−102.8	170.3	766	0.005595	,,	615
−181.9	91.3	758	0.003789	,,	402
−194.7	78.5	759	0.003527	,,	371

$$K = K_1 + K_0\sqrt{\frac{\lambda_0'}{\lambda_0}} = 0.00031 + 10\sqrt{\frac{0.007639}{0.01503}} = 0.00038$$

The value of η at 0°C. obtained by the present author is compared with those obtained by other authors in Table 3. The present author's value, though a little too large, may be considered good. (The author adopted $\eta_0 = 1724\times10^{-7}$ for air.)

Table 3.

$\eta\times10^5$	Authors
840	Graham and Meyer
870	Paluj
841	Markowski
850	Volker
849	Vogel
856	Kanda

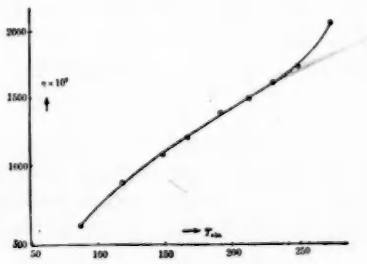

Fig. 2.

(3) *Fluorine.* The results are given in Table 4 and illustrated in Fig. 2.

$$\tau = 11.20\ \text{sec.},\quad \eta_0\,(\text{air}) = 1724\times10^{-7}.$$

$$K = 0.00031 + 10\sqrt{\frac{0.01816}{0.01503}} = 0.00042$$

Table 4.

T	p	λ	K	$\eta\times10^{-7}$
273.2	763	0.01816	0.00942	2093
248.9	,,	0.01505	,,	1727
229.6	,,	0.01407	,,	1611
213.1	765	0.01221	,,	1492
192.3	,,	0.01210	,,	1379
167.9	,,	0.01059	,,	1201
148.8	758	0.00957	,,	1080
118.9	,,	0.00783	,,	875
86.8	,,	0.00512	,,	555

V. Determination of the Diameter of Fluorine Molecule, etc. From the foregoing value of the viscosity, we get Sutherland's constant of fluorine, $C=129$.

As for the diameter of the molecule, we have $d=3.02$Å from

$$d^2 = 4.56\times10^{-20}\sqrt{M}\,/\,\eta_0\left(1+\frac{C}{273.2}\right).$$

Magat[2] obtained $b=3.4$Å.

The author got the mean free path

$$L = 9.12\times10^{-6}\text{cm.} \quad \text{from } L=\frac{1}{N\pi\sqrt{2}}\frac{1}{d^2}.$$

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(2) Magat, *Z. physik. Chem.*, B, **16** (1932), 1.